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IMPROVED FLUORINE-CONTAINING CATION EXCHANGE MEMBRANE
[改良された含フッ素陽イオン交換膜]

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SPECIFICATION

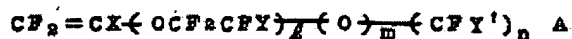
1. Title of the Invention

IMPROVED FLUORINE-CONTAINING CATION EXCHANGE MEMBRANE

2. Claims

- (1) a cross-linked fluoride containing cation exchange membrane which is comprised of a copolymer of a vinyl ether (I) which contains iodine which is expressed by
- $$\text{I}(\text{CF}_2)_p\text{O}(\text{CF}_2\overset{\text{CF}_3}{\text{CF}_2}\text{O})_q(\text{CF}_2\overset{\text{CF}_3}{\text{CF}_2}\text{O})_r\text{CF}=\text{CF}_2$$
- (here, p denotes 2~9, q, 0~5, and r, 0~5), and a fluoridated olefin (II), and a fluoride containing monomer (III) which has functional groups which are exchangeable with ion exchange groups or said group.
- (2) A membrane as in Claim (1) wherein the fluoridated olefin (II) is a compound that is expressed by $\text{CF}_2 = \text{CZZ}^1$ (here, Z, Z^1 are fluorine, chlorine, hydrogen or $-\text{CF}_3$).
- (3) A membrane as in Claim (1) in which there is a fluoride containing monomer (III) which has an ion exchange group or exchangeable group for said

group which is a compound that can be expressed by the general formula



(Here, X is fluorine or $-CF_3$, Y and Y' are perfluoroalkyl group of fluorine or carbon number 1~10, and in addition, A is an ion exchange group, $-SO_3H$, $-COOH$, $-PO_2H_2$, $-\phi OH$ (ϕ is allyl group), $-C(CF_3)_2OH$ or a group which is exchangeable with the ion exchanges groups of these. l is 0~3, m is 0 or 1, and n is 0~12).

- (4) A membrane as in Claims 1, 2, or 3 wherein for within the copolymer, the content of the vinyl ester (I) containing iodine is 0.1 ~10 mol
- (5) A membrane as in Claims 1, 2, 3, or 4 wherein for within the copolymer, the content weight of the fluorine monomer which has an ion exchange group or exchangeable group for said group is 1~50 mol.

3. Detailed Explanation of the Invention

This invention, in addition to relating to electrochemical substances, is related to a fluorine containing ion exchangeable group which has improved mechanical properties, and furthermore, more specifically, is related to a cross-linked fluoride containing cation exchange membrane which is comprised of a copolymer of a vinyl ether (I) which contains iodine which is expressed by



(here, p denotes 2~9, q, 0~5, and r, 0~5), and a fluoridated olefin (II), and a fluoride containing monomer (III) which has functional groups which are exchangeable with ion exchange groups or said group. Conventionally, as can be seen from Patent S48-20788 or S48-41942, practical use is provided an ion exchange membrane which is comprised of a copolymer of tetrafluoridated ethylene and perfluorovinyl ether containing a sulfonic acid group or a carbonic acid group. However, when there is use as an alkali electrolytic gap membrane of a positive ion exchange membrane which is comprised of copolymers of

perfluorovinyl ether and tetra fluoric ethylene, the electrochemical properties show comparative superior properties, but there is recognition that over long periods, there are large dimensional changes or wrinkles, and there is the conclusion that these long period effects contribute to the shortening of the useful life of the positive ion exchange membrane.

This invention as a positive ion exchange membrane which is comprised of a copolymer of tetrafluoric ethylene and perfluorovinyl ether does not possess a reduction in such electrochemical properties, and from the results of various investigations, which necessarily controlled the generation of dimensional changes or wrinkles during practical use, found that with a positive ion exchange membrane containing the cross-linked structure which is obtained from copolymers which are comprised of simple weight compositions as specified above, give the invention's goal.

In this invention, the iodine containing vinyl ester (I) which has, as the general formula which is used,



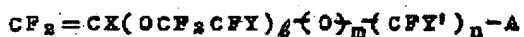
(here, p denotes 2~9, q, 0~5, and r, 0~5), is indispensable for achieving the above-mentioned goal of this invention, and even with an iodine containing compound, without the above-mentioned structure, not only are the above-mentioned mechanical properties not achieved, but there is also a degradation in the electrochemical properties. The iodine containing vinyl ester (I) which is used in this invention is constructed by well-known methods, for example, by the methods which are cited in Patent S45-8205.

The fluoridated olefin (II) which is used in this invention is expressed by, desirably, the following formula $CF_2 = CZZ^1$ (here, Z, Z^1 are fluorine, chlorine, hydrogen or $-CF_3$), and the following can be cited as representative examples:

tetrafluoridated ethylene, trifluoridated ethylene chloride, sextafluoridated propylene, trifluoridated ethylene, fluoridated pyridine, and fluoric vinyl. Above all, perfluoro compounds are desirable, and

especially, tetra fluoridated ethylene is the most suitable.

Furthermore, the fluoridated monomer (III) which has a functional group as an ion exchange group or which can be exchanged into an ion group which is used in this invention is desirable and can be expressed by the following general equation



l denotes 0~3m m, 0~1, n, 0~12, and X denotes fluorine or CF₃, Y and Y' denote fluorine or a perfluoroalkyl group of C1~10. In addition, A denotes the following ion exchange group, SO₃H, -COOH, -PO₂H₂, -φOH (φ is alyl group), -C(CF₃)₂OH or a group which is exchangeable with the ion exchanges groups of these, for example, -SO₂F, -SO₂Cl, -CN, -COF, -COOR (R is a 1~10 alkyl group), -COOM (M is an alkali metal or 4th class ammonium salt). These fluoridated monomers (III) are constructed by well-known arbitrary methods, methods cited in the specifications of Patents 3282875 and S45-22327. The copolymer of vinyl ester containing iodine mentioned above, the fluoridated olefin (II) and the

fluorine containing monomer which has an ion exchange group or a group which can be exchanged for an ion exchange group is obtained, by using or not using inactive organic solvents or aqueous mediums, from peroxy compounds, azo compounds, and from the peripherally known to the well-known methods polymerization means of polymerization initiation sources equivalent to ultraviolet rays and ionizing radiation.

The contents weight of the vinyl ester (I) which has iodine within the copolymer is desirably, 0.1 ~10 mol %, and especially desirable in the range of 0.5~5 mol %. In addition, the contents weight within the copolymer of the fluoridated monomer (III) which has an ion exchange group or a group which can be exchanged for an ion exchange group is related to the membrane's ion exchange's contents weight, desirably at 1~50 mol %, and especially desirable when selected from the range of 5~25 mol %.

Cross-linkage is performed for the above-mentioned copolymer, normally, before cross-linking, desirably, the membrane is formed. The means of membrane formation is performed by well-known arbitrary means, such as, press molding, rolling, extruding, liquid

flow extension, dispersion or pulverization. The thickness of the membrane that is molded is desirably is 20~1,000 μm , and better at 50~500, and in addition, the transmissive amount, with a column of water 10m (within pH 10, 4N NaCl aqueous solution at 60 °C), it is desirable to be less than 100ml/hr/m², and especially desirable at less than 10ml/hr/m². In addition, the exchange amount of the positive ion exchange membrane changes according to the amount of the fluoridated monomer (III), and especially when used as a gap membrane for alkali chloride electrolytes, it is desirable to have 0.5 ~ 2.5 milli equivalents /gram dried, and especially 0.7 ~ 2.0 mm/ gram dried.

The copolymer is formed by continuing the above process for a long time or the cross-linking of the copolymer of this invention is effected by well-known or lesser well-known methods which are used for the cross-linking of normal linear polymer such as heat, ultraviolet rays or radiation. For example, the method of heating at approximately 250 °C, and eliminating the iodine that was generated through reduced pressure was adopted. After the previous phase of the above-mentioned membrane formation or

cross-linking process, desirably, there is continuation of both processes, and the polymer is not the ion exchange membrane, and when there is a functional group which can replace said group, the functional groups are exchanged with the ion exchange group by water dispersion or intermediate reaction processing.

The positive ion exchange membrane which is comprised of this invention's fluoridated copolymer is used in a wide range of disparate field for properties which are superior electrically and mechanically.

For example the membrane is advantageously used, where durability is important, as a gap membrane for electrolytic reduction, fuel cells or diffusion penetration. When the membrane is used as a gap membrane for two chamber gap electrolysis for alkali chloride as mentioned above, superior properties are exhibited.

When electrolysis of the alkali chloride is performed using the fluoridated positive ion exchange membrane of this invention, as a means of manufacturing the alkali hydroxide solution, any of the well-known methods may be adopted. For example,

for the voltage and current density, these are respectively desirable at 2.3 ~5.5 volts, 5~ 100 A/dm² can be adopted. For the positive electrode which is used in electrolysis, it is possible to use a durable electrode which has dimension stability by coating an oxidized substance of the platinum metal family on the unleaded or titanium center. For example, on the positive ion exchange membrane of this invention, by separating the surfaces between the positive and negative electrodes, form a positive electrode chamber and a negative electrode chamber, and perform electrolysis by supplying an aqueous alkali chloride solution to the positive electrode chamber, and even with the two chamber formation which obtains the alkali hydroxide solution from the negative electrode, with raw materials of potassium chloride of concentration more than twice minimum required value, by performing electrolysis at current densities and temperatures of 50~90 °C, 5~50 A/dm², and with potassium hydroxide solution of high concentration of more than 40%, there is effective low electrolysis voltage and high current density, and furthermore, membrane degradation does not occur,

and there can be manufacture in which there is dimension stability for the long term.

Below, there are cited working examples in order to show concretely this invention, and this invention is, of course, not limited to the above-mentioned or below-mentioned working examples.

Moreover, the exchange capacity of the fluoridated positive ion exchange membrane is obtained as follows. That is, there is an exchange of the H-positive ion exchange membrane completely for H- by conducting in 1N of HCl for 5 minutes at 60 °C, and then wash with sufficient water so that there is no more remaining HCl. Afterwards, blend into a solution which has resulted from adding 0.5g of said H-membrane to 0.1N NaOH 25ml, and there is a complete exchange with the Na⁺. Next, taking the membrane, obtain the result by reverse titrating the amount of the NaOH within the solution using 0.1N hydrochloric acid.

Working Example 1

To a 200ml stainless steel reaction container add 37.5g of



and 6.3g of $\text{CF}_2 = \text{CFO} (\text{CF}_2)_4 \text{I}$, 31.5 g of trichlorotrifluorethane and 140mg of azo bis isobutyronitrile. After sufficiently deaerating with liquid nitrogen, make the reaction container 70 °C. Next, perform the reaction by putting up to 10.5kg/cm² of the tetra fluoridated ethylene. After, 20 hours, obtain a white-colored copolymer. The contents of $\text{CF}_2 = \text{CFO} (\text{CF}_2)_4 \text{I}$ within said copolymer was 2.6 mol % from the mass balance. By pressing said copolymer at 200 °C, after obtaining a film of 200µm thickness, the film was left standing at 250 °C, and while eliminating the iodine that had been generated under reduced pressure, the membrane was maintained for 6 hours, as cross-linking progressed. An ion exchange membrane of a dried membrane of functional weight 0.79 milli equivalents/g was obtained by water disassembling said membrane.

Using said ion exchange membrane, under the same conditions, perform saline electrolysis. Using Rh-Ti for the positive electrode and stainless steel for the negative electrode, assemble a two chamber electrolysis [Illegible] (the distance between the electrodes is 2.2 cm, and the membrane effective surface area 25 cm²).

In the positive electrode chamber, with 4N NaCl aqueous solution 150 cc, the concentration of the NaOH which is obtained in the negative electrode chamber, while supplying respectively water of a specified amount so as to make 4N, electrolysis is performed with an electric current density of 20A/dm², and liquid temperature 85 °C. When the result is 8N NaOH, the current efficiency is 70%. After continuously performing for 3 months, said ion membrane has changed dimensions of 0.7%, and hardly any wrinkles.

On the other hand, after using the 3 months in a solution under identical conditions for an ion exchange membrane of functional weight 0.78 milli equivalents/g which was obtained by copolymerization of only tetra fluoridated ethylene and



there was a 4.5% dimensional change and many wrinkles.

Working Example 2

In a stainless steel reaction container 200ml place 39.0 g

of $\text{CF}_2 = \text{CFO}(\text{CF}_2)_3\text{COOCH}_3$ and 5.3g of $\text{CF}_2 = \text{CF}(\text{CF}_2)_4\text{I}$ and 20mg of azobis isobutyronitrile. After sufficiently deaerating with liquid nitrogen, make the reaction container 70 °C. Next perform the reaction until there is 19.5 Kg/cm² of the tetra fluoridated ethylene. During the reaction maintain the pressure at 19.5 Kg/cm² while introducing the tetra fluoridated ethylene within the system during the reaction. After 5 hours, 6.9g of the copolymer is obtained. The amount of the $\text{CF}_2 = \text{CFO}(\text{CF}_2)_4\text{I}$ was 2.2 mol % from the mass balance.

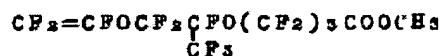
After letting a film form of 200μ thickness of said copolymer at 200 °C, maintain said film at 250 °C,

and while eliminating the iodine that was generated under reduced pressure, maintain for 6 hours at the same time that cross-linking is progressing. There is obtained an ion exchange membrane of functional capacity 1.45 equivalents/g by added water disassembly of said film. Using said ion membrane, in the same way as with Working Example 1, there is obtained electrolysis of table salt. With 14N of NaOH obtained, the current efficiency was 93%. After continuously performing electrolysis for 3 months, the dimensional change was 0.8%, with hardly any wrinkles.

On the other hand, under the same electrolysis conditions, when using an ion exchange membrane of functional capacity 14.5 milli equivalents/g that was obtained by copolymerizing only tetra fluoridated ethylene and $\text{CF}_2 = \text{CFO}(\text{CF}_2)_3\text{COOCH}_3$, there was a 4% dimensional change and wrinkles generated.

Working Example 3

Copolymerize tetra fluoridated ethylene and



and $\text{CF}_2=\text{CF}(\text{CF}_2)_4\text{I}$ under copolymerization conditions that are identical to Working Example 2, after a certain time, there is obtained an ion exchange membrane of functional capacity 1.29 milli equivalent/g dried membrane at 2.9% mol $\text{CF}_2=\text{CF}(\text{CF}_2)_4\text{I}$ by cross-linking. Using said ion membrane, when performing electrolysis in the same way as in Working Example 1, there was a dimensional change of 0.7% in 3 months giving a current efficiency of 92% having obtained 14N NaOH, with few wrinkles.

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